

KIESELGUHR

PATENT SPECIFICATION

640,115



Date of Application and filing Complete Specification: March 18, 1948.

No. 8107/48.

Application made in United States of America on June 11, 1947.

Complete Specification Published: July 12, 1950.

Index at acceptance:—Class 2(iii), C3a(5c: 13a3), C3a14a(1b : 8a).

COMPLETE SPECIFICATION

Synthesis of Oxygenated Organic Compounds

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the production of oxygenated organic compounds by the reaction of olefins with hydrogen and carbon monoxide and more specifically to the preparation of improved olefinic feed stocks for processes of this type. In particular, the invention refers to the production of oxygenated organic compounds from olefins obtained by the catalytic conversion of carbon monoxide and hydrogen and to improvements in the preparation of such olefins for the purpose of producing oxygenated organic compounds therefrom.

It is well known in the art that oxygenated organic compounds may be synthesized from olefins or diolefins by a reaction with carbon monoxide and hydrogen in the presence of catalysts containing cobalt, iron, nickel or the like in a two-step process in which predominantly aldehydes and ketones and minor proportions of alcohols are formed in a first step in the presence of the catalysts mentioned above and the product from the first step is hydrogenated in a second step to convert aldehydes and ketones into the corresponding alcohols. The catalyst used in the first stage may be employed in the second stage. However, other known hydrogenation catalysts may be used in the latter stage such as metallic nickel, nickel supported on kieselguhr, and others. The catalyst for the first stage usually contains promoters such as thoria, magnesia and the like.

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The alcohols produced by this process normally contain one more carbon atom than the olefin used as the starting material, the position of the added hydroxyl group depending on the positions of the double bond in the olefins. The olefins to be used as starting material may therefore be selected as a function for the purpose for which the product alcohol is desired.

For example, a detergent such as sodium lauryl sulfate may be prepared from an olefin such as undecene-1 by the alcohol synthesis. Other olefins and diolefins such as ethylene, propylene, butylene, pentenes, hexenes, butadiene, pentadienes, olefin polymers, such as di-isobutylene, triisobutylene, polybutylenes and olefinic fractions from thermal or catalytic cracking operations and other sources may be used as starting material depending on the nature of the aldehydes and alcohols desired. The olefins fed may comprise pure olefins or hydrocarbon mixtures containing olefins. In general, olefins having from 2 to 18 carbon atoms and more particularly from 8 to 18 carbon atoms, in the molecule are preferred.

The synthesis gas mixture containing hydrogen and carbon monoxide may be produced from any conventional sources such as carbonaceous solids or gases in any manner known *per se* and in any desired ratio of hydrogen to carbon monoxide. Ratios of 0.5 volume of hydrogen to 4.0 volumes of hydrogen per volume of carbon monoxide may be employed, about 1.0 volume of hydrogen per volume of carbon monoxide being preferred. The reaction of the olefins with H₂ and CO is generally conducted at pressures in the range of about 100 to 300 atmospheres and temperatures in the range of about 150° F. to 450° F.

The quantity of H₂ + CO with respect to olefins used may vary within wide ranges, for example from 1000 to 45,000 cu. ft. of H₂ + CO per barrel of

olefin fed. In general, approximately 2,500 to 15,000 cu. ft. of $H_2 + CO$ per barrel of olefin feed are employed. In the hydrogenation step temperatures are 5 generally within the range of from about 150° F. to 450° F. while pressures within the range of about 100 to 300 atmospheres are suitable.

The catalysts for the first stage of the 10 process are usually employed in the form of salts of the catalytically active metal with high molecular weight fatty acids such as stearic, palmitic, oleic, naphthenic, linoleic, and similar acids of 15 natural or synthetic origin. For example, metal soaps such as cobalt stearate, nickel oleate, cobalt naphthenate, and iron linoleate are suitable catalysts. These salts are soluble in the liquid olefin feed 20 and may be supplied to the reaction zone in the form of hydrocarbon solutions or dissolved in the olefin feed.

Prior to the present invention, attempts have been made to utilize as 25 starting materials for the process described above, olefins produced by the catalytic conversion of carbon monoxide with hydrogen over catalysts such as iron promoted with alkali metal compounds, or similar promoters. However, these 30 attempts have not been successful because olefin conversion in the first olefin oxygenation stage and selectivities toward the formation of alcohols are so low that 35 the process based on synthetic olefins of this type becomes uneconomical. It is the principal object of the present invention to provide a procedure by which this difficulty may be overcome and synthetic 40 olefins may be converted into useful starting material for the production of oxygenated organic compounds by the conversion of such olefins with carbon monoxide and hydrogen.

Investigations have indicated that the 45 difficulties arising in connection with the use of synthetic olefins as starting materials for the production of oxygenated organic compounds are connected 50 with the presence of certain oxygenated compounds particularly acidic materials introduced into these olefins by the original synthesis reaction. Therefore, the invention relates in its broadest aspect 55 to the production of oxygenated organic compounds from synthetic olefins which have been subjected to a treatment adapted substantially completely to free said olefins of synthetic acidic materials.

More specifically, the process of the 60 invention comprises a treatment of synthetic olefins with an alkaline treating agent, preferably with the hydroxides or oxides of the alkali or alkaline earth 65 metals whereby acidic constituents are re-

moved from the olefins, and the use of the thus purified olefins for the production of oxygenated organic compounds by the catalytic reaction with carbon monoxide and hydrogen. The alkaline treating 70 materials may be employed in solution or in solid form at normal atmospheric or elevated temperatures. For example, caustic soda solutions of 1 to 20 per cent, preferably 3 to 15% are suitable for the 75 purposes of the invention at treating temperatures of about 50° to 300° F. preferably about 50° to 100° F. It has been found that the yields of oxygenated organic compounds and the alcohol selectivities of the process using synthetic 80 olefins alkali-treated in accordance with the present invention are satisfactory for commercial operation.

The present invention will be best 85 understood from the more detailed description hereinafter wherein reference will be made to the accompanying drawing, the single figure of which is a 90 schematic illustration of a system suitable for carrying out a preferred embodiment of the invention.

Referring now in detail to the drawing, the numeral (5) indicates a conventional fluid type catalytic synthesis reactor for the conversion of carbon monoxide with hydrogen in the presence of finely divided synthesis catalyst. Reactor (5) contains a dense turbulent fluidized mass (3) of a synthesis catalyst, preferably an iron catalyst such as sintered pyrites ash promoted with about 1.5 per cent of potassium fluoride. Synthesis feed gas containing carbon monoxide and hydrogen is supplied from line (1) to reactor (5) at a suitable synthesis pressure of 5 to 50 atmospheres, preferably 15 to 40 atmospheres. The synthesis temperature may be maintained within the approximate limits of 500° to 800° F., 110 preferably between about 550° and 700° F. by conventional methods of heat removal (not shown). Other details of the operation of fluid synthesis reactors using iron catalysts are well known and 115 need not be further specified here.

The total product of the synthesis reaction is withdrawn from reactor (5) through line (7) and passed to a conventional gas solids separator (9) wherein 120 entrained catalyst fines may be separated from the product vapors and gases and returned through return pipe (11) to the catalyst mass (3) in reactor (5). Product vapors and gases substantially free of entrained catalyst are passed through line (13) to a separator (15) wherein the separation of liquids and gases and of a hydrocarbon layer from an aqueous layer is accomplished by cooling and settling. 130

Gas is withdrawn overhead through line (17) to be either recycled to reactor (5) or passed to a conventional gas recovery plant (not shown). The aqueous layer 5 containing the water-soluble oxygenated products is withdrawn from the bottom of separator (15) through line (19).

The total liquid hydrocarbon oil product containing olefins and oil-soluble 10 organic compounds is withdrawn from an upper liquid layer within separator (15) and passed through line (21) to a conventional fractionating column (23). The hydrocarbons are fractionated in column 15 (23) so as to recover heavy bottoms withdrawn through line (25) and an olefinic fraction of the boiling range desired for the production of oxygenated organic compounds. This fraction preferably has 20 a relatively narrow boiling range of about 50° to 100° F., falling within the approximate limits of 100° to 600° F., preferably 250° to 400° F., depending on the molecular weight and character of the 25 oxygenated compounds desired as the final product of the process.

The overhead from fractionator (23) passes through line (27) to a condenser (29) and from there in liquid form 30 through line (31) to the alkali treating chamber (35). The treating chamber (35) preferably contains a porous packing of refractory materials or the like such as Raschig rings, Berl saddles, etc.

An alkaline solution of the desired 35 strength is supplied to treating chamber (35) from alkali storage tank (37) through lines (39) and/or (41). Treating chamber (35) is preferably maintained at a temperature of 50° to 300° F. and may be operated at any desired pressure. On 40 their way through treating chamber (35) the olefinic feed and the alkaline treating solution are thoroughly mixed in any 45 conventional manner and intimately contacted so as to assure substantially complete removal of the acids contained in the hydrocarbon feed in the form of organic salts of the metal of the alkaline 50 treating agent.

A mixture of treated hydrocarbons and 55 spent treating agent is withdrawn from treating chamber (35) through line (43) and passed to a settler (45) wherein it is separated into an aqueous bottom layer and oil top layer. The aqueous bottom layer containing excess alkaline treating agent and organic salts of its metal is withdrawn through line (47) and passed 60 to an organic acid regenerator (49) wherein it is treated with a strong inorganic acid, preferably sulfuric acid to set free the organic acids. The acid mixture is passed from regenerator (49) 65 through line (50) to a settler (51) wherein

it is separated into a top layer containing the crude organic acids which may be withdrawn through line (53) and a bottom layer containing the neutral inorganic salt produced in regenerator (49). 70 The bottom layer may be discarded through line (55).

Returning now to settler (45) the hydrocarbon layer is withdrawn through line (57) and dried in drier (59) with conventional drying agents such as calcium chloride, alumina, or other dehydrating agents and/or adsorbents. 75

The dried liquid olefinic hydrocarbons pass from drier (59) through line (61) to 80 a pipe (63) wherein they are mixed with a catalyst promoting the conversion with carbon monoxide and hydrogen into oxygenated organic compounds. Any conventional type catalyst such as cobalt 85 stearate or naphthenate may be used in proportions varying between about 0.1 and 5.0 per cent by weight of olefins. The mixture of olefinic feed stock and catalyst is passed to an upper portion of primary 80 reactor (65) to be converted into oxygenated organic compounds primarily aldehydes and ketones.

Simultaneously, a gas mixture containing hydrogen and carbon monoxide in the 95 approximate ratio of 0.5—2.0 volumes of hydrogen per volume of carbon monoxide is supplied through line (67) to the bottom portion of primary reactor (65). Reactor (65) is preferably operated at a pressure 100 of about 3000 pounds per square inch and at a temperature of about 250° to 400° F. Liquid and gases flowing countercurrently through reactor (65) are intimately contacted therein. Unreacted gas 105 is withdrawn overhead through line (69), scrubbed in scrubber (71) of entrained liquid and catalyst in the form of metal carbonyl, and preferably recycled through line (73) to gas feed line (67). 110

Liquid oxygenated reaction products and unreacted olefins are withdrawn from a bottom portion of reactor (65) through line (75) and passed to a catalyst removal zone (77) which is packed with a catalytic 115 ally inert solid material such as ceramic Raschig rings, kieselguhr, pumice, charcoal or silica gel, etc. Hydrogen recovered from a later stage of the process, as will appear hereinafter, may be supplied to zone (77) through line (79) and passed through zone (77) countercurrently to the liquid oxygenated product. Catalyst removal zone (77) is preferably maintained at a temperature of about 200° to 125 450° F. at which the catalyst which enters zone (77) predominantly in the form of metal carbonyl dissolved in the liquid product is decomposed into metal and carbon monoxide. The metal is de- 130

posed on the inert packing within zone (77) while the carbon monoxide is purged by the hydrogen. A mixture of hydrogen and carbon monoxide is withdrawn 5 through line (81) either to be discarded through line (83) or to be passed through line (85) to a methanizer (87) wherein the carbon monoxide is converted thermally or catalytically into methane in any conventional manner. The methane and hydrogen may be passed through line (89) to hydrogenation reactor (95). The liquid oxygenated product now free of oxygenation catalyst is withdrawn 15 from zone (77) through line (91) and passed to a bottom portion of hydrogenation reactor (85). Simultaneously, hydrogen is supplied to reactor (95) through line (93) in proportions sufficient to convert the aldehydes and ketones contained 20 in the oxygenated feed into the corresponding alcohols. Reactor (95) contains a mass (97) of any conventional hydrogenation catalyst. For example, when 25 nickel is employed as the hydrogenation catalyst, reactor (95) may be operated at pressures ranging from about 300 to 3000 pounds per square inch, at temperatures of about 300° to 400° F. and at an H₂ rate of about 5000 to 20,000 normal cu. ft. per bbl. of feed. The catalyst may be employed in the form of fixed or moving beds, or it may be suspended in the liquid feed. Details of hydrogenation 30 processes of this type are well known in the art and need not be further specified. Unreacted hydrogen may be withdrawn overhead from reactor (95) through line (99) and either vented through line (100) or recycled through line (102) via lines (79) and/or (103) to the catalyst removal zone (77), as previously described, or hydrogenation reactor (95). The hydrogenated product stream is 45 withdrawn from reactor (95) through line (105). This product which is now highly concentrated in the desired alcohols may be passed to any conventional product recovery plant (not shown). The system illustrated by the drawing 50 permits of various modifications. Fixed or moving bed reactors may be used in place of fluid synthesis reactor (5) in any manner known *per se*. Other synthesis catalysts promoting the formation of liquid olefins from carbon monoxide and hydrogen may replace the iron catalysts specified. The alkaline treating agent in 55 treating chamber (35) may be solid rather than a liquid. Other conventional oxygenating catalysts than those specified 60 may be supplied to line (63). For example, insoluble finely divided metal catalysts may be used in aqueous or oil suspension. Instead of nickel, other

hydrogenation catalysts such as tungsten, or sulfides of metals of groups VI and VIII of the periodic table may be utilized.

The invention will be further illustrated by the following specific examples. 70

EXAMPLE I.

An olefinic feed stock was prepared as follows:

A total hydrocarbon product was synthesized by passing a feed consisting primarily of hydrogen and carbon monoxide in a volume ratio of 2:1 over an iron catalyst containing 1.5% alumina and about 1.5% potassia at 650° F. and 400 psig. This product was fractionated in conventional apparatus and a fraction boiling in the range of 250°—300° F. was collected for further treatment.

Inspection of this fraction showed the following values:

Gravity, "A.P.I."	-	-	-	53.4
Hydroxyl number	-	-	-	9
Carbonyl number	-	-	-	274
Saponification number	-	-	-	42
Acid number	-	-	-	32.8
Bromine number	-	-	-	92

A sample of this fraction was treated with 5 per cent caustic soda solution at 70°—90° F. for 12 minutes. The treated product showed the following inspection data:

Gravity, "A.P.I."	-	-	-	56.5
Hydroxyl number	-	-	-	23
Carbonyl number	-	-	-	33
Saponification number	-	-	-	100
Acid number	-	-	-	0.9
Bromine number	-	-	-	88

The estimated olefin content was changed from about 73% in the untreated fraction to about 70 per cent in the treated fraction.

A sample of the untreated fraction was reacted in an autoclave with CO and H₂ at the conditions and with the results given below using a catalyst consisting of 31.2% Co, 0.9% Cu, 5.6% ThO₂, 62.3% Silica.

	Aldehyde	Stage	115
Catalyst Concentration, Wt. %	11		
Volume Ratio H ₂ /CO in Gas	1.2		
Duration of Test, Hours	5		
Temperature, °F.	275		
Pressure, psig.	3000	120	
Olefin Conversion, Wt. %	16		
Gravity of Product, "A.P.I."	49.8		

Because of the extremely low yield of oxygenated product the latter was not subjected to hydrogenation.

A sample of the alkali treated fraction was converted using the same catalyst at the conditions and with the results given below:

		Aldehyde Stage	Hydrogenation Stage
5	Catalyst Concentration, Wt. %	12	20°
	Volume Ratio H_2/CO in Gas	1.2	—
	Duration of Test Hours	5	12
	Temperature, °F.	275	350
	Pressure, psig.	3000	2700
10	Olefin Conversion, Wt. %	86	—
	INSPECTION OF PRODUCT		
	Gravity, *A.P.I.	37.3	—
	Hydroxyl Number	36	210
	Carbonyl Number	197	1
15	• Nickel on Kieselguhr used as catalyst in hydrogenation stage.		

A comparison of the results reported above indicates that the treatment of the synthetic olefins with alkali in accordance with the present invention leads to about a 5-fold increase in olefin conversion.

EXAMPLE II.

A synthetic olefin fraction boiling between 350° and 400° F. was obtained 25 from an oil produced as described in Example I.

This fraction had the following inspection data:

30	Gravity, *A.P.I.	41.7
	Hydroxyl number	18
	Carbonyl number	112
	Saponification number	46
	Acid number	34.8
	Bromine number	54

35 A sample of this fraction was treated with a 10 per cent caustic soda solution at a temperature of 70°—90° F. for 12 minutes. The treated sample showed the following inspection data:

Gravity, *A.P.I.	44.3	40
Hydroxyl number	17	—
Carbonyl number	33	—
Saponification number	13	—
Acid number	0.1	—
Bromine number	57	45

The estimated olefin content was changed by the alkali treatment from about 58% in the untreated fraction to about 61% in the treated fraction.

A sample of the untreated fraction was 50 converted with hydrogen and carbon monoxide using the oxygenation catalyst specified in Example I at the conditions and with the results given below.

	Aldehyde Stage	Hydrogenation Stage
	11	11
Catalyst Concentration, Wt. %	1.2	—
Volume Ratio, H_2/CO in Gas	5	—
Duration of Test, Hours	350	60
Temperature, °F.	3000	—
Pressure, psig.	6	—
Olefin Conversion, Wt. %	40.4	—
Gravity of Product, *A.P.I.		

using the same catalyst at the conditions and with the results given below.

	Aldehyde Stage	Hydrogenation Stage
70	9	9
Catalyst Concentration, Wt. %	1.2	—
Volume Ratio of H_2/CO in Gas	5	12
Duration of Test, Hours	350	350
Temperature, °F.	3000	2700
Pressure, psig.	77	—
Olefin Conversion, Wt. %		
INSPECTION OF PRODUCT		
Hydroxyl Number		150
Carbonyl Number		2

80 • The oxygenation catalyst was used in the hydrogenation stage.

A comparison of the above results shows that the alkali treatment of these synthetic olefins in accordance with the present invention permits about a 13-fold 5 increase of the olefin conversion into oxygenated products.

It should be understood that the slight deviations in the oxygenation conditions of the experiments reported above have 10 little or no influence on olefin conversion.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we 15 claim is:—

1. A process for producing oxygenated organic compounds by the catalytic conversion of CO and H₂ to olefins in the presence of a hydrocarbon synthesis 20 catalyst and the subsequent treatment of the said olefins with CO and H₂ in the presence of an oxygenation catalyst under oxygenation conditions, wherein the olefins are treated with an alkaline 25 treating agent to remove acidic materials therefrom before being subjected to the oxygenation treatment.

2. The process according to Claim 1, in which said treating agent is an oxide or 30 hydroxide of an alkali or alkaline earth metal.

3. The process according to Claims 1 or 2, in which said treating agent comprises caustic alkali.

35 4. The process according to any of Claims 1 to 3, in which said alkaline treating agent is in the form of an aqueous solution.

5. The process according to Claim 4, 40 in which the aqueous solution contains about 3—15% of NaOH.

6. The process according to any of Claims 1 to 5, in which said olefins are treated with said treating agent at temperatures of 50° to 300° F.

45 7. The process according to any of Claims 1 to 6, in which said oxygenated compounds are hydrogenated in the presence of a hydrogenation catalyst and at hydrogenation conditions of temperature and pressure conducive to the conversion of aldehydes and ketones contained in said materials into the corresponding alcohols.

55 8. The process according to any of Claims 1 to 7, in which said hydrocarbon synthesis catalyst is an iron-type catalyst and said catalytic conversion is carried out at temperatures of about 500°—800°

F. and pressures of about 5—50 atmospheres.

9. The process of producing oxygenated organic compounds which comprises contacting a gas mixture containing CO and H₂ in synthesis proportions at synthesis conditions of temperature and pressure with a synthesis catalyst promoting the formation of normally liquid olefinic hydrocarbons at said synthesis conditions, recovering synthetic olefins, 65 treating said recovered olefins with an alkaline treating agent at conditions adapted to neutralize organic acids contained in said olefins to form organic salts, separating said salts from said olefins, contacting said separated olefins with CO and H₂ at oxygenation conditions of temperature and pressure and in the presence of an oxygenation catalyst, adapted to convert said olefins into oxygenated compounds, and recovering said oxygenated compounds.

10. The process according to any of Claims 1 to 9, in which said synthesis catalyst is an iron-type catalyst, said synthesis temperature is about 500°—800° F., said synthesis pressure about 5—50 atmospheres, and said synthesis proportions about 0.5 to 4 volumes of H₂ per volume of CO.

90 11. The process according to Claims 9 or 10 in which said synthetic olefins are recovered by distilling the total product of said synthesis reaction.

12. The process according to Claim 11, in which said distilled mixture of synthetic olefins has a boiling range between 100° and 600° F.

13. The process according to Claims 11 or 12, in which the said synthetic olefins have a fifty to one hundred degree boiling range within the temperatures from 250° to 400° F.

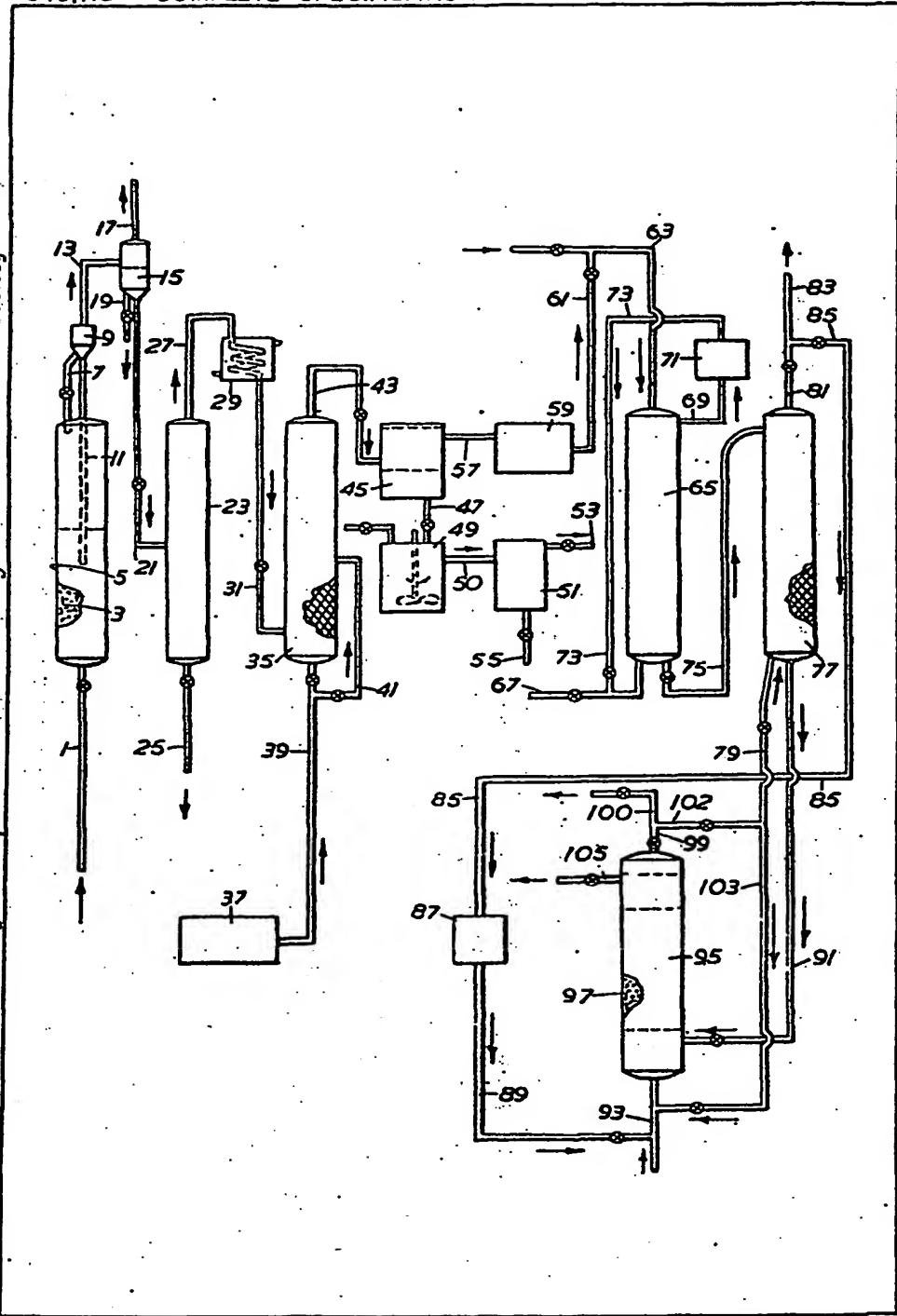
14. The process according to any of Claims 9 to 13, in which said salts are converted with a strong inorganic acid into organic acids and inorganic salts of said inorganic acids and said organic acids are recovered.

15. The process according to any of the preceding claims, in which the olefins are dried prior to their contact with the CO and H₂.

Dated this 18th day of March, 1948.

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[This Drawing is a reproduction of the Original on a reduced scale.]



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